3rd International Symposium on Green Chemistry
May 3-7, 2015 - La Rochelle - FRANCE

N°827 / OC - FC - PC

Biomass conversion - Chemical valorization of wastes

BIO-BASED NITRILES VIA HETEROGENEOUSLY CATALYZED OXIDATIVE DECARBOXYLATION OF AMINO ACIDS

Laurens Claes / KU Leuven - Centre for Surface Chemistry and Catalysis, Kasteelpark Arenberg 23, 3001 Heverlee
Dirk De Vos / KU Leuven - Centre for Surface Chemistry and Catalysis, Kasteelpark Arenberg 23, 3001 Heverlee
Roman Matthessen / KU Leuven - Centre for Surface Chemistry and Catalysis, Kasteelpark Arenberg 23, 3001 Heverlee
Ine Rombouts / KU Leuven - Laboratory of Food Chemistry and Biochemistry, Kasteelpark Arenberg 20, 3001 Heverlee
Ivo Stassen / KU Leuven - Centre for Surface Chemistry and Catalysis, Kasteelpark Arenberg 23, 3001 Heverlee
Trees De Baerdemaeker / KU Leuven - Centre for Surface Chemistry and Catalysis, Kasteelpark Arenberg 23, 3001 Heverlee
Diederik Depla / Ghent University - Department of Solid State Sciences, Krijgslaan 281(S1), 9000 Gent
Jan Delcour / KU Leuven - Laboratory of Food Chemistry and Biochemistry, Kasteelpark Arenberg 20, 3001 Heverlee
Bert Lagrain / KU Leuven - Centre for Surface Chemistry and Catalysis, Kasteelpark Arenberg 23, 3001 Heverlee

ABSTRACT

Increasing amounts of proteins are available as waste streams from agro-industry and biofuel production. Although the average protein content of these byproducts varies from 20 to 40 wt%,[1] this fraction is rarely used for industrial applications. Hydrolytic depolymerization, as an essential part of waste protein valorization into bio-based chemicals, results in aqueous mixtures of amino acids; further separation is demanding due to their zwitterionic nature.[2] Here, oxidative decarboxylation of amino acids into nitriles is proposed as a useful link in the valorization chain, because it not only provides a way around the separation issue, but even allows to recycle nitrogen into - often bifunctional - nitrile platform molecules. For instance, nitriles give access to amines, amides, acids. The reaction is generally mediated by hypobromite ('Br+') species, which are often produced from halogenated reagents like N-bromosuccinimide,[3] or by NaOCl induced oxidation of NaBr,[4] together with large amounts of (in)organic waste. On the other hand, bromoperoxidases catalyze this transformation using H_2O_2 as oxidant, but selectivity is difficult to control.[5]

A heterogeneous catalytic system was developed to mimic the halide oxidation activity of these enzymes. Proximity effects exerted by the layered double hydroxide (LDH) supported tungstate catalyst facilitate both halide oxidation[6] and subsequent decarboxylation.[7] Selective defunctionalization of amino acids into nitriles is achieved in aqueous media using catalytic amounts of bromide and H_2O_2 as green oxidant. Many naturally occurring amino acids were converted with excellent selectivity, often resulting in yields > 90% (Figure 1). The system is compatible with alcohols, amides, and even carboxylic acids, amines or guanidines after an appropriate neutralization step; methionine can be transformed into a nitrile-sulfone derivative. In addition, this system was successfully applied to convert wheat gluten, as an example of a protein-rich byproduct from the starch industry, into useful bio-based N-containing chemicals, thereby demonstrating the potential for closing the N-loop.

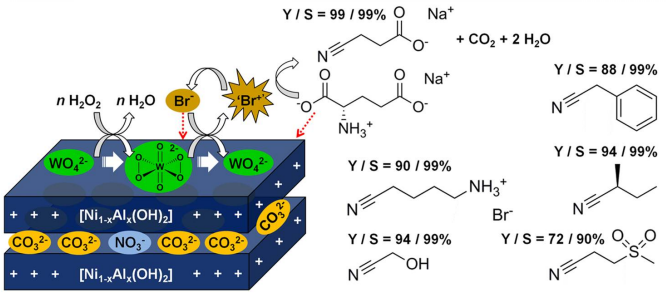

FIG1 LEGEND

Figure 1. Heterogeneous catalytic system for oxidative decarboxylation of amino acids.

FIG2 LEGEND

KEYWORDS

amino acids | biomass | decarboxylation | heterogeneous catalysis | nitriles

REFERENCES

[1] T.M. Lammens, M.C.R. Franssen, E.L. Scott, J.P.M. Sanders, Biomass Bioenerg. 2012, 44, 168-181.
[2] Y. Teng, E.L. Scott, A.N.T. van Zeeland, J.P.M. Sanders, Green Chem. 2011, 13, 624-630.
[3] G. Laval, B.T. Golding, Synlett 2003, 4, 542-546.
[4] J. Le Nôtre, E.L. Scott, M.C.R. Franssen, J.P.M. Sanders, Green Chem. 2011, 13, 807-809.
[5] A. But, J. Le Nôtre, E.L. Scott, R. Wever, J.P.M. Sanders, ChemSusChem 2012, 5, 1199-1202.
[6] B. Sels, D. De Vos, M. Buntinx, F. Pierard, A. Kirsch-De Mesmaeker, P. Jacobs, Nature 1999, 400, 855-857.
[7] L. Claes, R. Matthessen, I. Rombouts, I. Stassen, T. De Baerdemaeker, D. Depla, J.A. Delcour, B. Lagrain, D.E. De Vos, ChemSusChem, accepted.

Dirk.DeVos@biw.kuleuven.be